Population Transfer to a Predissociating Target State Using Pulsed Coherent Excitation: Sensitivity to Coupling to Background States†

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We have examined the sensitivity to the presence of background states of population transfer to a predissociating molecular state generated by coherent two-pulse excitation. The system studied is intended to model optical control of the formation of a product in a photofragmentation reaction. The model spectrum of states is a generalization of the three-state spectrum considered in the conventional STIRAP method in three respects: the target state is a resonance in the continuum, the spectrum includes both unoccupied background states that have finite lifetimes and some unoccupied pairs of background states that are in resonance with the excitation pulses, and nonadiabatic population transfer is allowed. We examine the variation of the population transfer to the target state with respect to its lifetime, as well as the robustness of the population transfer with respect to variation of the area of overlap of the two excitation pulses and with respect to the presence of background states (some of which have finite lifetimes). Our results show that there is a broad range of conditions under which it is possible to transfer population efficiently from an initial state to a target predissociating state using coherent two-pulse excitation, although that population transfer is not always adiabatic.

1. Introduction

Optical control of the selection of the products of a reaction has received considerable attention in recent years.[1] There are several different ways of implementing optical control of molecular dynamics, all derived from the same basic principles. Although these methods are independent of the size of the system to be controlled, accurate predictions of the character of the control field become increasingly difficult as the number of degrees of freedom increases. For example, the multidimensionality and complicated topography of the potential energy surfaces of a large polyatomic molecule make it very difficult to use pulse timing control of product selection in a unimolecular reaction because the evolution of a wave packet on a complicated potential energy surface is difficult to visualize and follow. The multipath interference control of product selection in a unimolecular reaction of a large polyatomic molecule becomes more difficult as the number of states per unit energy interval increases because the identification of suitable pairs of pathways between the same initial and the final states requires detailed knowledge of the character of all states involved, including those associated with competitive excitations. As argued elsewhere,[1] it is desirable to have a reduced-states representation[2,3] within which one can describe the control process.

Among its other attributes, we regard the STIRAP (stimulated Raman adiabatic passage)[4−21] and the extended STIRAP[22−24] methods of control of population transfer to be examples of reduced-states descriptions of molecular dynamics in the sense that they use a stationary-state representation. In this representation, the members of a subset of active states between which population transfer is to be generated are directly coupled only by the applied fields. All other states of the system can be coupled to the active subset of states only by off-resonance dipole-allowed transitions.

The STIRAP method, in its simplest form, uses two suitably timed coherent pulses of light coupling a three-state system that has nonvanishing transition moments connecting state $|1\rangle$ to state $|2\rangle$ and state $|2\rangle$ to state $|3\rangle$ but has zero transition moment between states $|1\rangle$ and $|3\rangle$. The excitation process is designed to transfer all of the population initially in state $|1\rangle$ to state $|3\rangle$. The field associated with the pump pulse, $\mathcal{E}_p$, that couples the initial state $|1\rangle$ to the intermediate state $|2\rangle$, and the field associated with the Stokes pulse, $\mathcal{E}_S$, that couples $|2\rangle$ to the final state $|3\rangle$ are large enough to generate many cycles of Rabi oscillation between $|1\rangle$ and $|2\rangle$ and between $|2\rangle$ and $|3\rangle$, respectively. The coherent field−matter eigenstates can be represented as linear superpositions of the bare matter states $|1\rangle$, $|2\rangle$, and $|3\rangle$ and the system wave function as a linear combination of the coherent field−matter eigenstates. Selective population transfer from bare matter state $|1\rangle$ to bare matter state $|3\rangle$ is generated by varying the contributions of the coherent field−matter eigenstates to the system wave function; this is accomplished through control of the ratio of Rabi frequencies. There is a range of values of the parameters that define the pump and Stokes pulses for which adiabatic transfer of population from state $|1\rangle$ to state $|3\rangle$ accompanies this variation when they are counterintuitively ordered, with the Stokes pulse preceding but overlapping the pump pulse. Criteria for variation of the Rabi frequencies that satisfy the condition of adiabatic transfer of population can be found in the literature;[4] they contain constraints on both the strengths and the rates of change of the Stokes and pump fields. Studies of the influence on the population transfer of the nonadiabaticity of the excitation process,[5,6] of the detuning of the pump and Stokes pulse frequencies from resonance with the intermediate state,[5,8] and

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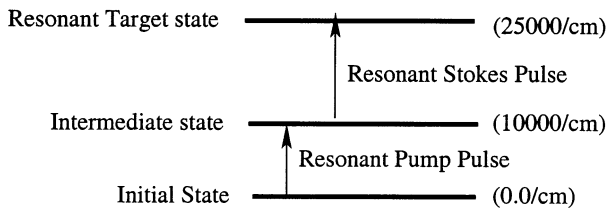

Figure 1. Schematic diagram of the three-state system.

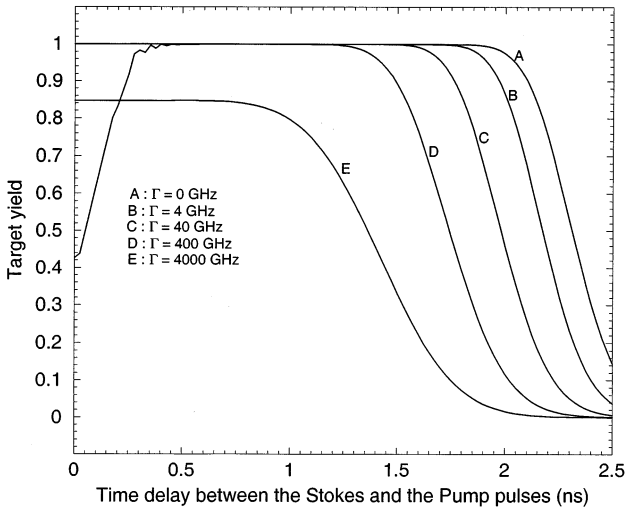

Figure 2. Plot of the variation of the target predissociating state yield versus the time delay between the counterintuitively ordered Stokes and pump pulses in the absence of background states.

of the existence of multiple intermediate and final states[9−11] have also been reported.

Furthermore, several extensions of the original STIRAP method of population transfer have been reported.[21−25] A sequential STIRAP method has been proposed for controlling an isomerization reaction (HCN ↔ CNH) that cannot be controlled by a simple STIRAP process.[25] It has been shown that it is possible to achieve efficient population transfers between initial and final bound states in systems in which the intermediate states are resonances embedded in the continuum.[26−30] In these cases, efficient adiabatic population transfer occurs provided that the pulse duration is shorter than the lifetime of the intermediate state. It is now accepted that complete population transfer from an arbitrary initial state to a selected target state in a ladder-like distribution of energy states is possible using a suitable set of overlapping pulses provided that the lifetimes of the target states are longer than the pulse durations. In addition, it is possible to use an extended STIRAP method for selective population transfer from an initial state to one of two degenerate final states, which thereby permits control of product selectivity in branching unimolecular reactions.[22−24]

Given the success of the STIRAP method for efficient population transfer, we are interested in extending the use of coherent superpositions of states to include nonadiabatic processes that can generate efficient and selective population transfer. This short paper is concerned with the efficiency of two-photon-induced population transfer from an initial state to a target state that predissociates, i.e., the target state can be described as a resonance in the continuum.[22] An early study of the relative importance of incoherent and coherent processes in stepwise multiphoton-induced photodissociation by Ackerholt and Eberly[31] established a condition under which molecular coherence can be neglected. The establishment of this condition starts with the observation that the Rabi frequency is the geometric mean of the stimulated transition rate and the absorption line width. It states that, if the rates of the transitions between the successive states involved in the multiphoton pathway increase as the energy increases and if every stimulated transition rate populating a state exceeds the rates of all decay processes that depopulate that state, then all coherent Rabi oscillations are damped, and the overall transfer of population from the initial state to the dissociating state can be treated as an incoherent process. Key roles in this argument are played by the assumption concerning the monotonic increase of the stimulated transition rate with increasing energy and the assumption that the final step, the rate of fragmentation (or ionization), can be made arbitrarily large. These constraints are rather restrictive, as shown by an investigation by Frishman and Shapiro[32] of one-photon-induced population transfer from an initial bound state to a state that is a resonance in a continuum. Their analysis reveals that, when a strong short pulse is used, the irreversible transition to the resonance state characteristic of weak-field excitation can be replaced by reversible multiple transitions that execute Rabi oscillations between the initial bound state and the resonance state. These Rabi oscillations are similar, but not identical, to those between two bound states. In principle, when there are multiple overlapping resonances in the continuum, there can be interference between transitions from the initial state to these resonances. Because a one-photon-induced population transfer from a bound state to a state that is a resonance in a continuum is the final process in the Ackerholt−Eberly analysis, we conclude that coherence effects are likely to be important over some range in which the resonance width exceeds the Rabi frequency.

The process we consider in this paper is different from that considered by Frishman and Shapiro in three respects. First, as already mentioned, instead of one-photon excitations, we consider two-photon excitations that generate efficient population transfer to a predissociating state. Second, we do not limit attention to the case in which the population transfer is adiabatic, i.e., we find non-STIRAP mechanisms for population transfer. Third, we are concerned with the influence of background states on the two-pulse coherent-field-induced population transfer. Aspects of the reverse of the process we examine, two-photon-enhanced recombination of atoms, have been studied by Vardi, Abrashkevich, Frishman, and Shapiro.[33] They analyzed the induced recombination of atoms into a molecule when the atoms were illuminated with two coherent laser pulses, the first exciting the free atoms to a long-lived intermediate molecular (predissociating) state whose lifetime is limited by spontaneous emission and the second resonant with the energy difference between that intermediate state and a bound molecular state. The scheme is, in effect, a reverse-STIRAP process. Indeed, it is found that very efficient recombination is generated when the counterintuitive pulse sequence is used, i.e., the pulse that is resonant with the energy difference between the intermediate and bound molecular states precedes but overlaps the pulse that excites the free atoms to the intermediate state. This pulse sequence was found to be more efficient at generating molecules than the sequence with intuitive ordering of pulses because the efficiency of the latter is limited by spontaneous emission from the intermediate state. To avoid such spontaneous loss in the case of counterintutive ordering of the pulses used, the pulse duration must be shorter than the lifetime of the intermediate state.

The system studied in this paper consists of three active states embedded in a spectrum of many states. The target state in our system has a finite lifetime, to model a molecular state that undergoes predissociation; the initial and intermediate states are

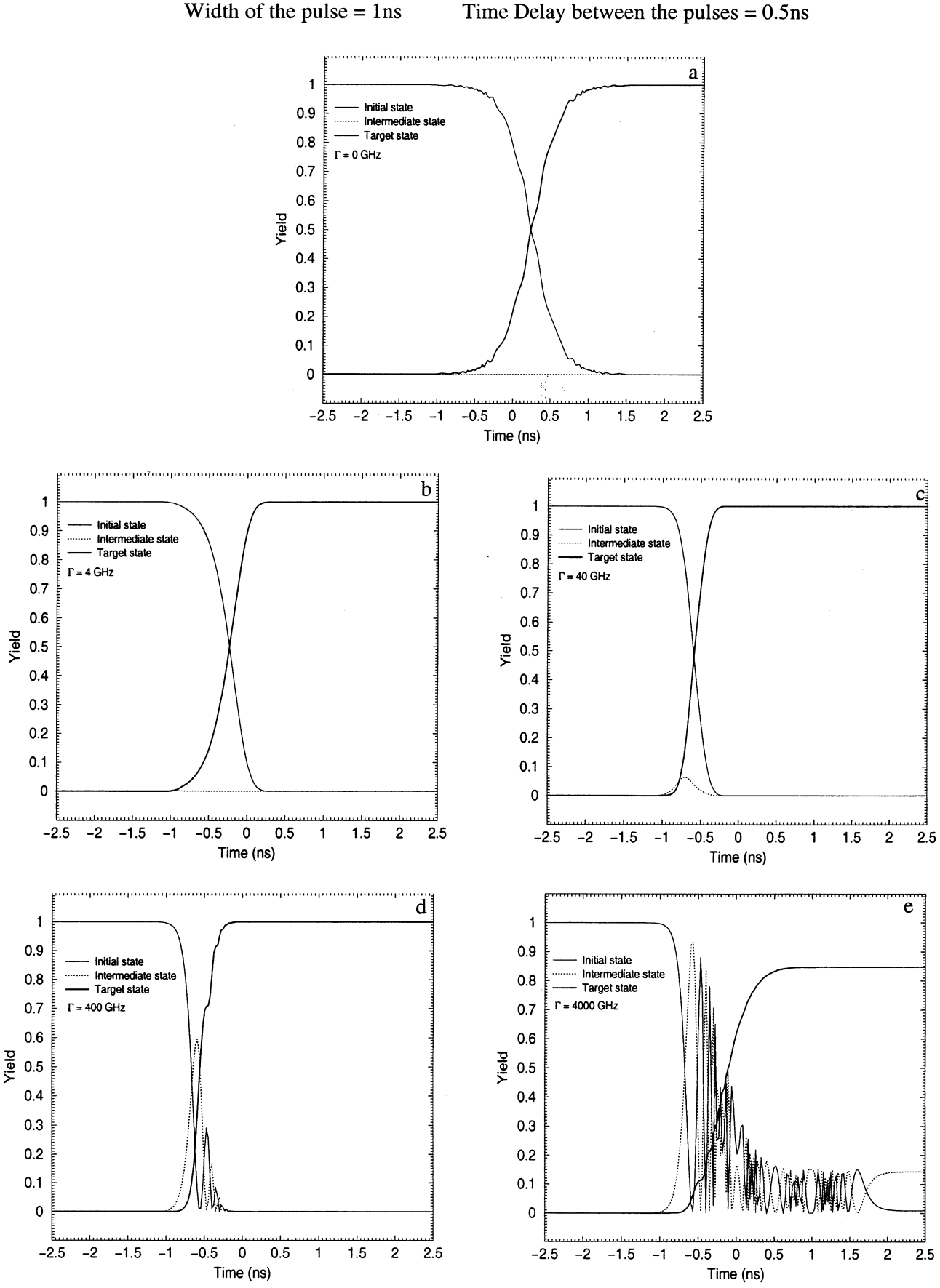

Figure 3. Plot of the variation of the population transfer to different states as a function of time for a fixed width of the pump and Stokes pulses and a fixed time delay between the pulses in the absence of background states. (a) $\Gamma_3 = 0$ GHz, (b) $\Gamma_3 = 4$ GHz, (c) $\Gamma_3 = 40$ GHz, (d) $\Gamma_3 = 400$ GHz, (e) $\Gamma_3 = 4000$ GHz.

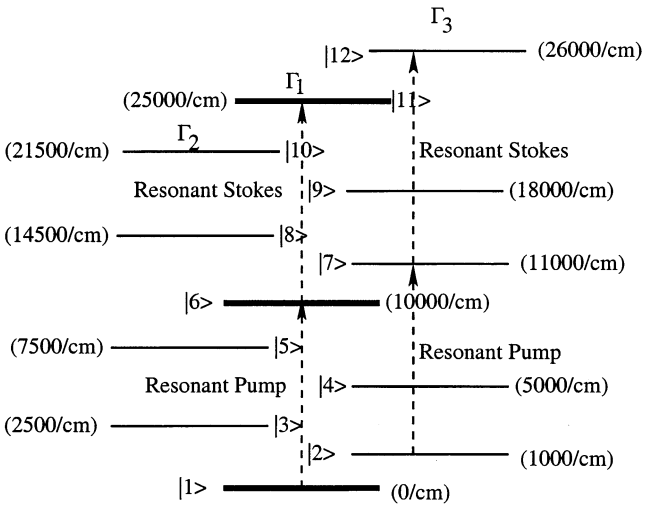

Figure 4. Schematic diagram of the three-state system and the background states considered.

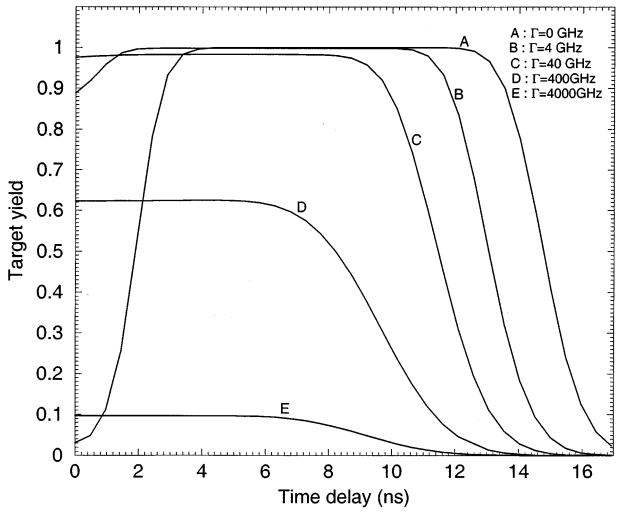

Figure 5. Plot of the variation of the population transfer to the target predissociating state versus the time delay between the counterintuitively ordered Stokes and pump pulses in the presence of background states.

assumed to be bound states with infinite lifetimes. Some of the unoccupied background states also have finite lifetimes, and some unoccupied pairs of background states are assumed to be in resonance with the frequencies of the excitation pulses. The original stimulus for this investigation was the observed robust character of STIRAP-generated population transfer. However, because we do not require that the desired population transfer in our system be adiabatic, our analysis is not limited to cases where the conditions for STIRAP are met. We examine the variation of the population transfer to the target state with respect to its lifetime, as well as the robustness of the population transfer with respect to variation of the area of overlap of the two excitation pulses and with respect to the presence of background states (some of which have finite lifetimes). Our results show that there is a broad range of conditions under which it is possible to transfer population efficiently from an initial state to a target predissociating state using coherent two-pulse excitation, although that population transfer is not always adiabatic.

2. Methodology

A formal basis for ascribing a complex energy to a predissociating state can be developed from complex scaling of the system Hamiltonian; discussions of this methodology can be found in the literature.[34,35] For a three-state system in which state $|3\rangle$ is a resonance embedded in a continuum while states $|1\rangle$ and $|2\rangle$ are bound, the complex scaled Hamiltonian in the absence of the coupling can be written in the form

$$H_\theta = \begin{vmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 - i\Gamma_3/2 \end{vmatrix} \quad (1)$$

where E_i is the real component of the energy of state i and Γ_i is its imaginary part. We now introduce an electric field consisting of two pulses, which we label the pump and Stokes pulses to make contact with the formalism of STIRAP. The pump pulse couples the initial state to the intermediate state, whereas the Stokes pulse couples the intermediate state to the target resonance. The Hamiltonian can then be written as

$$H_\theta = \begin{vmatrix} E_1 & -\Omega_p \exp(-i\phi_p)\cos(\omega_p t) & 0 \\ -\Omega_p \exp(i\phi_p)\cos(\omega_p t) & E_2 & -\Omega_S \exp(-i\phi_S)\cos(\omega_S t) \\ 0 & -\omega_S \exp(i\phi_S)\cos(\omega_S t) & E_3 - i\Gamma_3/2 \end{vmatrix} \quad (2)$$

where Ω_p and Ω_S are the Rabi frequencies and ω_p and ω_S are the Bohr frequencies of the pump and Stokes pulses, respectively. After absorption of the pump and Stokes field phase shifts into the basis states, the Hamiltonian takes the form

$$H_\theta = \begin{vmatrix} E_1 & -\Omega_p \cos(\omega_p t) & 0 \\ -\Omega_p \cos(\omega_p t) & E_2 & -\Omega_S \cos(\omega_S t) \\ 0 & -\omega_S \cos(\omega_S t) & E_3 - i\Gamma_3/2 \end{vmatrix} \quad (3)$$

In the following sections, we discuss population transfer in this model system as a function of the decay rate (resonance width) of the target state in the absence and presence of background states.

3. Population Transfer to a Predissociating Target State in the Absence of Background States

A schematic diagram of the three-state model system is shown in Figure 1. The eigenstates of H_θ were calculated by transforming to the interaction representation, so that $\exp(i\phi_i)\,|i\rangle \rightarrow \exp[i(E_i t + \phi_i)]\,|i\rangle \equiv \psi_i(t)$, and the time-independent phase shift is preserved. In this new representation, H_θ takes the form

$$\begin{vmatrix} 0 & -\Omega_p \cos(\omega_p t) e^{[-i(E_2 - E_1)t]} & 0 \\ -\Omega_p \cos(\omega_p t) e^{[-i(E_2 - E_1)t]} & 0 & -\Omega_S \cos(\omega_S t) e^{[-i(E_3 - E_2)t]} \\ 0 & -\Omega_S \cos(\omega_S t) e^{[-i(E_3 - E_2)t]} & -i\Gamma/2 \end{vmatrix} \quad (4)$$

Making the rotating wave approximation and exploiting the consequences of the resonances between the pump and Stokes frequencies and the transition frequencies, we find

$$H_\theta = -\frac{1}{2}\begin{vmatrix} 0 & \Omega_p & 0 \\ \Omega_p & 0 & \Omega_S \\ 0 & \Omega_S & i\Gamma \end{vmatrix} \quad (5)$$

It is possible to construct analytic solutions for the eigenvalues and eigenvectors of this model system, but they are very complicated and offer no immediate insight into the nature of the excitation process. Instead of using the analytic forms, we solved the time-dependent Schrödinger equation numerically using a fourth-order Runge−Kutta integrator.

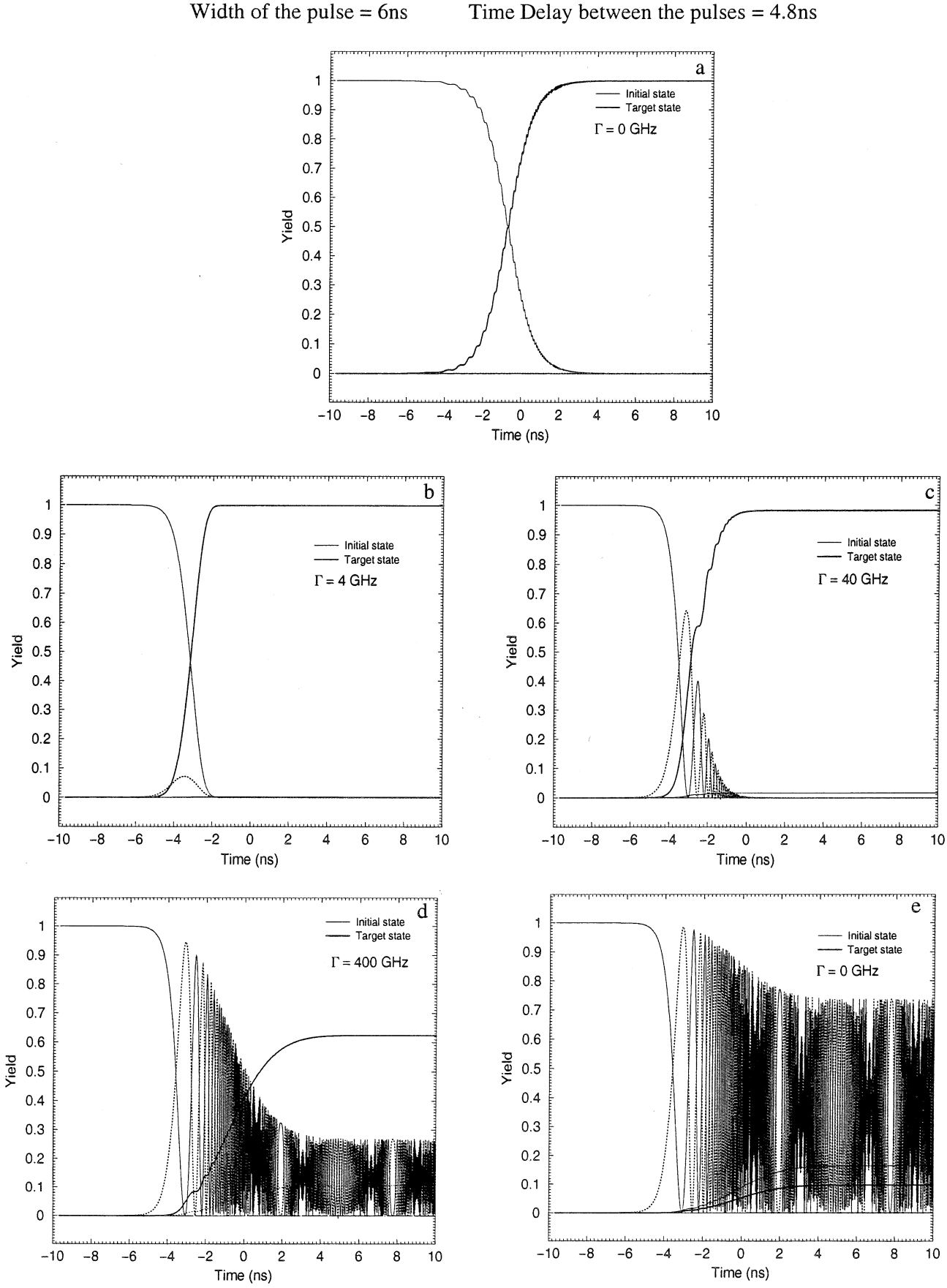

Figure 6. Plot of the variation of population transfer to different states as a function of time for a fixed width of the pump and Stokes pulses and a fixed time delay between the pulses in the presence of background states. (a) $\Gamma_{11} = 0$ GHz, (b) $\Gamma_{11} = 4$ GHz, (c) $\Gamma_{11} = 40$ GHz, (d) $\Gamma_{11} = 400$ GHz, (e) $\Gamma_{11} = 4000$ GHz.

TABLE 1: Field Parameters

	intensity (W/cm^2)	frequency (au)	fwhm (ns)
pump pulse	3.17×10^8	0.045 56	1.0
Stokes pulse	3.17×10^8	0.068 35	1.0

TABLE 2: Variation of the Target Yield with Respect to the Width of the Pulses for Different Decay Rates of the Resonant Target State

	target state yield (%)				
pulse width (ns)	$\Gamma_3 =$ 0 GHz	$\Gamma_3 =$ 4 GHz	$\Gamma_3 =$ 40 GHz	$\Gamma_3 =$ 400 GHz	$\Gamma_3 =$ 4000 GHz
1.0	99.97	99.77	77.61	14.85	1.6
1.5	98.72	99.77	89.98	23.93	2.7
2.0	87.63	99.165	93.24	30.31	3.57
2.5	66.96	98.0	95.11	36.0	4.41
3.0	56.2	96.905	96.27	41.06	5.22
3.5	34.0	96.2	96.98	45.64	6.02
4.0	24.66	95.83	97.41	49.74	6.79
4.5	18.90	95.75	97.66	53.40	7.55
5.0	15.61	95.84	97.81	56.7	8.28
5.5	13.89	96.025	97.90	59.68	9.0
6.0	11.42	96.26	97.95	62.33	9.7

The Rabi frequencies of both the Stokes and the pump pulses were fixed at 40 GHz, and both widths were taken to be 1 ns. The transition dipole moments coupling the inital and intermediate states and the intermediate and target states were assumed to be 0.1 au. The field strengths for the Gaussian pulses associated with the resonant transitions are shown in Table 1. These choices for the Rabi frequencies and transition dipole moments limit the field strengths to less than that which excites competing multiphoton processes. The calculations were performed using the counterintutitive time sequence for the pulses. The target state yield is determined from the integral

$$Y_i = \int_0^t d\tau \langle \psi_i(\tau) \, |\Gamma_i| \psi_i(\tau) \rangle \tag{6}$$

which measures the population transferred in time t from the initial state to the target predissociating state $\psi_i(\tau)$ with decay rate Γ_i. A plot of the variation of the yield in the target state with respect to the time delay between the counterintuitively ordered Stokes and the pump pulses for different values of Γ_3 is shown in Figure 2. For a wide range of time delay and Γ_3 values, the yield in the target state is almost 100% (when $\Gamma_3 =$ 0, 4, 40, and 400 GHz), but it falls to around 85% when $\Gamma_3 =$ 4000 GHz. Note that, when Γ_3 is increased, the plateau in the yield versus time delay drops off at successively shorter time delays. For a Rabi frequency of 40 GHz, we obtain almost 100% population transfer to the target state for resonance widths up to 400 GHz, but when the resonance width is increased to 4000 GHz, the yield drops by almost 15%. We conclude from these calculations (that is, for the range of overlap of pump and Stokes pulses considered herein) that complete transfer of population to a predissociating target state in a three-state system using a two-pulse coherent excitation process can be achieved as long as one uses pulses with Rabi frequencies greater than one-tenth the resonance width. We have also observed that one can achieve almost 100% population transfer to the target predissociative state when $\Gamma_3 = 4$, 40, and 400 GHz even when the pump and Stokes pulses nearly coincide, which is not the case when the target state has infinite lifetime. We discuss this characteristic feature of the excitation process below.

We have examined the time dependence of the transfer of population to the intermediate and target states for fixed time delays between the pump and Rabi pulses (Figure 3). These calculations show that, when $\Gamma_3 = 0$, 4, and 40 GHz, the transfer of population to the intermediate state is either zero or negligibly small throughout the time required for transfer of population to the target state. However, when $\Gamma = 400$ and 4000 GHz, prior to completion of the transfer of population to the target state, there is considerable oscillatory transfer of population to and from the intermediate state and the initial state. For the case of $\Gamma = 400$ GHz, it is easily seen that the population of the target state increases monotonically with apparent shoulders at the peaks of the oscillations in the initial state population (and the troughs in the oscillations in the intermediate state population). This behavior is present but less clearly evident in the temporal dependence of the target population for the case of $\Gamma = 4000$ GHz. The temporal dependence of the target-state population in these cases suggests that the transfer of population to the target state is affected at the peaks of the oscillatory population of the intermediate state generated by Rabi oscillations between states $|1\rangle$ and $|2\rangle$. Clearly, for $\Gamma_3 > 40$ GHz and the other parameter values defined in the tables and figure captions, the transfer of population from the initial state to the target state is not adiabatic, and the mechanism thus differs from that associated with conventional STIRAP-generated population transfer.

4. Population Transfer to a Predissociative Target State in the Presence of Background States

The vibrational spectrum of a polyatomic molecule is usually rich in the energy range from which one might wish to select intermediate and target states with which to carry out a population transfer using a two-pulse coherent excitation process. Indeed, likely intermediate and target states might be coupled by dipole transitions to many background states, and each background state might be coupled similarly to yet other background states. Moreover, some of the transitions between the background states might be resonant with the Stokes and pump pulse frequencies. In this section, we report studies of the effect of coupling to and between background states on population transfer to a predissociating target state.

A schematic diagram of the energy levels considered and their energies is shown in Figure 4. Note that this model spectrum places two of the background states in the continuum energy regime; we assume that both of these resonances have a width of 4000 GHz. States $|1\rangle$, $|6\rangle$, and $|11\rangle$ are the original subset discussed in the preceding section. All of the other states shown have been incorporated to study the effect on the population transfer of background coupling. To study its influence on the population-transfer dynamics, we have assumed that, in addition to the resonant pump transition between states $|1\rangle$ and $|6\rangle$ and the resonant Stokes transition between states $|6\rangle$ and $|11\rangle$, there are also resonant pump transitions between background states $|2\rangle$ and $|7\rangle$ and resonant Stokes transitions between background states $|7\rangle$ and $|12\rangle$. The remainder of the transitions between states of the model spectrum are not resonant with either the pump or Stokes frequency.

The Hamiltonian for this set of calculations is a 12×12 matrix constructed using the rotating wave approximation. After reduction of the matrix elements associated with exact matches between the pump and Stokes field frequencies and the transition frequencies between pairs of states, we find eq 7,

$$H_\theta - \frac{1}{2}\begin{vmatrix} 0 & M_{1,2} & M_{1,3} & M_{1,4} & M_{1,5} & \Omega_p & M_{1,7} & M_{1,8} & M_{1,9} & M_{1,10} & M_{1,11} & M_{1,12} \\ M_{2,1} & 0 & M_{2,3} & M_{2,4} & M_{2,5} & M_{2,6} & \Omega_p & M_{2,8} & M_{2,9} & M_{2,10} & M_{2,11} & M_{2,12} \\ M_{3,1} & M_{3,2} & 0 & M_{3,4} & M_{3,5} & M_{3,6} & M_{3,7} & M_{3,8} & M_{3,9} & M_{3,10} & M_{3,11} & M_{3,12} \\ M_{4,1} & M_{4,2} & M_{4,3} & 0 & M_{4,5} & M_{4,6} & M_{4,7} & M_{4,8} & M_{4,9} & M_{4,10} & M_{4,11} & M_{4,12} \\ M_{5,1} & M_{5,2} & M_{5,3} & M_{5,4} & 0 & M_{5,6} & M_{5,7} & M_{5,8} & M_{5,9} & M_{5,10} & M_{5,11} & M_{5,12} \\ \Omega_p & M_{6,2} & M_{6,3} & M_{6,4} & M_{6,5} & 0 & M_{6,7} & M_{6,8} & M_{6,9} & M_{6,10} & M_{6,11} & \Omega_s \\ M_{7,1} & M_{7,2} & M_{7,3} & M_{7,4} & M_{7,5} & M_{7,6} & 0 & M_{7,8} & M_{7,9} & M_{7,10} & M_{7,11} & M_{7,12} \\ M_{8,1} & M_{8,2} & M_{8,3} & M_{8,4} & M_{8,5} & M_{8,6} & M_{8,7} & 0 & M_{8,9} & M_{8,10} & M_{8,11} & M_{8,12} \\ M_{9,1} & M_{9,2} & M_{9,3} & M_{9,4} & M_{9,5} & M_{9,6} & M_{9,7} & M_{9,8} & 0 & M_{9,10} & M_{9,11} & M_{9,12} \\ M_{10,1} & M_{10,2} & M_{10,3} & M_{10,4} & M_{10,5} & M_{10,6} & M_{10,7} & M_{10,8} & M_{10,9} & i\Gamma_{10} & M_{10,11} & M_{10,12} \\ M_{11,1} & M_{11,2} & M_{11,3} & M_{11,4} & M_{11,5} & M_{11,6} & M_{11,7} & M_{11,8} & M_{11,9} & M_{11,10} & i\Gamma_{11} & M_{11,12} \\ M_{12,1} & M_{12,2} & M_{12,3} & M_{12,4} & M_{12,5} & M_{12,6} & M_{12,7} & M_{12,8} & M_{12,9} & M_{12,10} & M_{12,11} & i\Gamma_{12} \end{vmatrix} \quad (7)$$

where $M_{nn'} = \exp[it(\omega_S - (E_n - E_n))]$. The transition dipole moments associated with the transitions that are resonant with the pump and Stokes frequencies were assumed to be 0.1 au; all other transition moments were set to 0.01 au. As already noted, the widths of the predissociative states $|10\rangle$ and $|12\rangle$ were set to 4000 GHz.

The efficiency of population transfer to the predissociative target state was calculated for $\Gamma_{11} = 4$, 40, 400, and 4000 GHz and different pulse widths with a fixed time delay of 1 ns between the pump pulse and the Stokes pulse. The population transferred to the target state for different pulse widths and for different resonance widths is shown in Table 2. We observe that the incorporation of background states into the model spectrum decreases the population transfer relative to that found in their absence. The variation in the population transfer with respect to variation of the width of the pulses for fixed time delay (equivalent to variation in the overlap of the pump and Stokes pulses) is displayed in Table 2. Clearly, for a fixed pulse separation, an increase in the width of the pulses increases the efficiency of population transfer to the predissociative target state. The most efficient population transfer achieved in this model spectrum occurs when the widths of the pump and Stokes pulses are 6 ns. We have not determined the efficiency of population transfer associated with pulse widths greater than 6 ns because the increase in computation time required became excessive with respect to our resources.

We now consider the variation of the efficiency of population transfer to the target state as a function of time delay between counterintuitively ordered pulses for the case in which the widths of the pump and Stokes pulses have the fixed value 6 ns. The results are shown in Figure 5. For $\Gamma_{11} = 0$ and 4 GHz, the transfer of population to the target state is almost 100%. For $\Gamma_{11} = 40$ GHz, the efficiency of population transfer drops to 97%, slightly smaller than was found in the absence of background states. Further increases of Γ_{11} lead to larger decreases in the efficiency of population transfer, to 63% for $\Gamma_{11} = 400$ GHz and to 10% for $\Gamma_{11} = 4000$ GHz. As in the case in which there are no background states, for $\Gamma_{11} > 40$ GHz, it appears that the transfer of population to the target state is affected at the peaks of the oscillatory population of the intermediate state generated by Rabi oscillations between states $|1\rangle$ and $|2\rangle$. Overall, the general dependence of the population transfer to the target state on the pulse time delay in the presence of background states is similar to that without the background states (Figure 6). We note that the time delay range for which the target yield is constant increases with increasing width of the pulses because of the larger area of overlap of the pulses. The trend observed suggests that overlap of the pump and Stokes pulses is an important factor when the population needs to be transferred to a predissociating target state. If the resonance widths are larger than the Rabi frequencies, the larger overlap of the pump and Stokes pulses facilitates population transfer to the predissociating target state from the peak population in the intermediate state.

5. Concluding Remarks

Our results indicate that it is possible to use two-pulse coherent excitation to achieve almost complete population transfer to a target predissociating state in the presence of background coupling. This efficient transfer occurs even when the Rabi frequencies of the pulsed fields used are equal to or moderately smaller than the decay rate of the predissociating state. When the Rabi frequencies are an order of magnitude or more smaller than the decay rate of the predissociating state, it is still possible to generate efficient population transfer to the target state without use of a field that forces the rate of transfer from the intermediate state to the target state to greatly exceed the rates of all other processes. In this limit, the population-transfer process is nonadiabatic and is not related to any STIRAP process.

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References and Notes

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